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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/EP95/02375 (22) International Filing Date: 19 June 1995 (19.06.95) (30) Priority Data: P 44 21 120.1 19 June 1994 (19.06.94) DE 195 03 170.9 1 February 1995 (01.02.95) DE (71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): BERNARD, Jean, Luc [FR/FR]; 51, rue André-Oudin, Giencourt, F-60600 Cler- mont (FR). DE MERINGO, Alain [FR/FR]; 294, rue Saint- Jacques, F-75005 Paris (FR). ROUYER, Elisabeth [FR/FR]; 32 bis, rue de l'Alma, F-92600 Asnières (FR). FURTAK, Hans [DE/DE]; Im Oberkämmerer 35, D-67346 Speyer am Rhein (DE). (74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 Munich (DE).</p>		<p>(81) Designated States: AU, BR, CA, CN, CZ, FI, HU, JP, KR, MX, NO, NZ, PL, SI, SK, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: MINERAL-FIBER COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>A biologically degradable mineral-fiber composition characterized by the following constituents in percent by weight: SiO₂: 45 to 60, Al₂O₃: less than 2, CaO 7: to 18, MgO: 4 to 10, Na₂O: 7 to 20, K₂O: 0 to 4, B₂O₃: 1 to 12, P₂O₅: 0 to 4, diverse: 0 to 5, Na₂O: + K₂O: 7 to 24, CaO + MgO: more than 15.5 and up to 25, BaO: 0 to 5, TiO₂: 0 to 4, Cr₂O₃: 0 to 1.5, Fe₂O₃: 0 to 3.</p>		

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Mineral-fiber compositions

The present invention relates to a mineral-fiber composition that is biologically degradable.

The prior art describes some mineral-fiber compositions which are said to be biologically degradable.

The biological degradability of mineral-fiber compositions is of great importance because various studies point out that mineral fibers with very small diameters in the range of less than 3 microns can be carcinogenic, while biologically degradable mineral fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the mineral fibers, or the products produced therefrom, the resistance of the mineral fibers and the processibility of the mineral-fiber composition.

For example mineral fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the mineral-fiber composition must permit processibility by known methods for producing mineral fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel mineral-fiber composition that is characterized by

biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a mineral-fiber composition that has considerable amounts of alkali oxides and alkaline-earth oxides, and optionally phosphorus oxide.

It has turned out that such a mineral-fiber composition fulfills the combination of the necessary properties, namely biological degradability, resistance to moisture and good processibility.

The object of the invention is a mineral-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO ₂	45	to 60
Al ₂ O ₃	less than 2	
CaO	7	to 18
MgO	4	to 10
Na ₂ O	7	to 20
K ₂ O	0	to 4
B ₂ O ₃	1	to 12
P ₂ O ₅	0	to 4
Diverse	0	to 5
Na ₂ O + K ₂ O	7	to 24
CaO + MgO	more than 15.5	and up to 25
BaO	0	to 5
TiO ₂	0	to 4
Cr ₂ O ₃	0	to 1.5
Fe ₂ O ₃	0	to 3.

The inventive mineral-fiber compositions are processible by the centrifugal technique. The obtained fibers have good resistance to moisture. Surprisingly enough, the mineral-fiber compositions show biological degradability. The mean fiber diameter is preferably 10 microns or less, and is in particular between 2.5 and 5 microns.

The inventive mineral-fiber compositions preferably have the following constituents in percent by weight:

SiO ₂	50	to 58
Al ₂ O ₃		less than 2
CaO	10	to 18
MgO	4	to 8
Na ₂ O	10	to 18
K ₂ O	0	to 2
B ₂ O ₃	3	to 12
P ₂ O ₅	0.5	to 4
Diverse	0	to 2
Na ₂ O + K ₂ O	10	to 21
CaO + MgO	16	to 24
BaO	0	to 4
TiO ₂	0	to 3
Cr ₂ O ₃	0	to 1
Fe ₂ O ₃	0	to 2.

The inventive mineral-fiber compositions have in particular the following constituents in percent by weight:

SiO ₂	50	to 57
Al ₂ O ₃	0.5	to 1.5
CaO	11	to 16
MgO	4.5	to 6
Na ₂ O	12	to 17

K ₂ O	0.5	to 1
B ₂ O ₃	5	to 11
P ₂ O ₅	1	to 3
Diverse	0.5	to 1.0
Na ₂ O + K ₂ O	11	to 17
CaO + MgO	16	to 22
BaO	0	to 3
TiO ₂	0	to 2
Cr ₂ O ₃	0	to 0.5
Fe ₂ O ₃	0	to 1.5.

The inventive mineral-fiber compositions preferably have less than 55% silicon dioxide.

It is also particularly preferred that the compositions contain more than 5 percent by weight, in particular more than 6 percent by weight, magnesium oxide.

Barium oxide is preferably added in exchange for calcium oxide.

Biological degradability can be increased by adding phosphorus pentoxide. The inventive compositions therefore preferably contain at least 0.5 percent by weight P₂O₅.

It is advantageous to add titanium oxide, chromium oxide and/or iron oxide to reduce the corrosive properties of the melt.

The moisture-resistance of the inventive mineral-fiber compositions was determined by a standard method known as the DGG method. In the DGG method 10 g finely ground mineral with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered.

red and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount of mineral dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested mineral.

The biological degradability of the inventive mineral compositions was tested by introducing 1 g of the mineral powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

NaCl	6.78
NH ₄ Cl	0.535
NaHCO ₃	2.268
NaH ₂ PO ₄ ·H ₂ O	0.166
(Na ₃ citrate) 2H ₂ O	0.059
Glycine	0.450
H ₂ SO ₄	0.049
CaCl ₂	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO₂ in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A composition was produced with the following constituents in percent by weight:

SiO ₂	56
Al ₂ O ₃	0.5
CaO	15
MgO	4.0
Na ₂ O	16.2
K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	1.5
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 32 mg/g was determined.

The above-described test for biological degradability yielded a value of 615.

Example 2

A composition was produced with the following constituents in percent by weight:

SiO ₂	54.5
Al ₂ O ₃	0.5
CaO	15
MgO	4.0
Na ₂ O	16.2

K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	3.0
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 32 mg/g was determined.

The above-described test for biological degradability yielded a value of 690.

Example 3

A composition was produced with the following constituents in percent by weight:

SiO ₂	56
Al ₂ O ₃	0.5
CaO	13
MgO	6
Na ₂ O	16.2
K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	1.5
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 32 mg/g was determined.

The above-described test for biological degradability yielded a value of 615.

Example 4

A composition was produced with the following constituents in percent by weight:

SiO ₂	54.5
Al ₂ O ₃	0.5
CaO	13
MgO	6
Na ₂ O	16.2
K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	3
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 32 mg/g was determined.

The above-described test for biological degradability yielded a value of 690.

Example 5

A composition was produced with the following constituents in percent by weight:

SiO ₂	56
------------------	----

Al ₂ O ₃	0.5
CaO	16
MgO	6
Na ₂ O	13.2
K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	1.5
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 22 mg/g was determined.

The above-described test for biological degradability yielded a value of 585.

Example 6

A composition was produced with the following constituents in percent by weight:

SiO ₂	54.5
Al ₂ O ₃	0.5
CaO	16
MgO	6
Na ₂ O	13.2
K ₂ O	0.8
B ₂ O ₃	5.5
P ₂ O ₅	3
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 22 mg/g was determined.

The above-described test for biological degradability yielded a value of 660.

Example 7

A composition was produced with the following constituents in percent by weight:

SiO ₂	54.5
Al ₂ O ₃	1
CaO	16
MgO	6
Na ₂ O	13.2
K ₂ O	0.8
B ₂ O ₃	6.5
P ₂ O ₅	1.5
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 17 mg/g was determined.

The above-described test for biological degradability yielded a value of 570.

Example 8

A composition was produced with the following constituents in percent by weight:

SiO ₂	53
Al ₂ O ₃	1
CaO	16
MgO	6
Na ₂ O	13.2
K ₂ O	0.8
B ₂ O ₃	6.5
P ₂ O ₅	3
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 17 mg/g was determined.

The above-described test for biological degradability yielded a value of 645.

Example 9

A composition was produced with the following constituents in percent by weight:

SiO ₂	50.5
Al ₂ O ₃	1.5
CaO	16
MgO	8
Na ₂ O	12.2

K ₂ O	0.8
B ₂ O ₃	6.5
P ₂ O ₅	4
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 7 mg/g was determined.

The above-described test for biological degradability yielded a value of 660.

Example 10

A composition was produced with the following constituents in percent by weight:

SiO ₂	50.5
Al ₂ O ₃	1.5
CaO	18
MgO	6
Na ₂ O	10.7
K ₂ O	0.8
B ₂ O ₃	8
P ₂ O ₅	4
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 7 mg/g was determined.

The above-described test for biological degradability yielded a value of 660.

Example 11

A composition was produced with the following constituents in percent by weight:

SiO ₂	55
Al ₂ O ₃	1
CaO	11
MgO	5
Na ₂ O	14.2
K ₂ O	0.8
B ₂ O ₃	11.5
P ₂ O ₅	1
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 31 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 12

A composition was produced with the following constituents in percent by weight:

SiO ₂	56.5
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Al ₂ O ₃	0.5
CaO	11
MgO	5
Na ₂ O	14.2
K ₂ O	0.8
B ₂ O ₃	10.5
P ₂ O ₅	1
Diverse	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 36 mg/g was determined.

The above-described test for biological degradability yielded a value of 620.

Example 13

A composition was produced with the following constituents in percent by weight:

SiO ₂	58.0
Al ₂ O ₃	0.5
CaO	13.0
MgO	7.0
Na ₂ O + K ₂ O	13.5
B ₂ O ₃	8.0.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 21 mg/g was determined.

The above-described test for biological degradability yielded a value of 515.

Example 14

A composition was produced with the following constituents in percent by weight:

SiO ₂	57.0
Al ₂ O ₃	0.5
Fe ₂ O ₃	1.0
CaO	13.0
MgO	7.0
Na ₂ O + K ₂ O	13.5
B ₂ O ₃	8.0.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 22 mg/g was determined.

The above-described test for biological degradability yielded a value of 480.

Example 15

A composition was produced with the following constituents in percent by weight:

SiO ₂	58.0
Al ₂ O ₃	0.5
CaO	9.5
MgO	7.0
Na ₂ O + K ₂ O	17.0
B ₂ O ₃	8.0.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 36 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 16

A composition was produced with the following constituents in percent by weight:

SiO ₂	58.0
Al ₂ O ₃	0.5
CaO	13.0
MgO	7.0
Na ₂ O + K ₂ O	17.0
B ₂ O ₃	4.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 27 mg/g was determined.

The above-described test for biological degradability yielded a value of 515.

Example 17

A composition was produced with the following constituents in percent by weight:

SiO ₂	57.5
Al ₂ O ₃	0.5
CaO	13.5
MgO	6.5
Na ₂ O + K ₂ O	17.0
B ₂ O ₃	4.5
Cr ₂ O ₃	0.5.

This mineral composition could be processed by the centrifugal technique.

Using the above-described DGG method a value of 25 mg/g was determined.

The above-described test for biological degradability yielded a value of 490.

Claims

1. A mineral-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO ₂	45	to 60
Al ₂ O ₃	less than 2	
CaO	7	to 18
MgO	4	to 10
Na ₂ O	7	to 20
K ₂ O	0	to 4
B ₂ O ₃	1	to 12
P ₂ O ₅	0	to 4
Diverse	0	to 5
Na ₂ O + K ₂ O	7	to 24
CaO + MgO	more than 15.5	and up to 25
BaO	0	to 5
TiO ₂	0	to 4
Cr ₂ O ₃	0	to 1.5
Fe ₂ O ₃	0	to 3.

2. The mineral-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	50	to 58
Al ₂ O ₃	less than 2	
CaO	10	to 18
MgO	4	to 8
Na ₂ O	10	to 18
K ₂ O	0	to 2

B ₂ O ₃	3	to 12
P ₂ O ₅	0.5	to 4
Diverse	0	to 2
Na ₂ O + K ₂ O	10	to 21
CaO + MgO	16	to 24
BaO	0	to 4
TiO ₂	0	to 3
Cr ₂ O ₃	0	to 1
Fe ₂ O ₃	0	to 2.

3. The mineral-fiber composition of claim 1 or 2, characterized by the following constituents in percent by weight:

SiO ₂	50	to 57
Al ₂ O ₃	0.5	to 1.5
CaO	11	to 16
MgO	4.5	to 6
Na ₂ O	12	to 17
K ₂ O	0.5	to 1
B ₂ O ₃	5	to 11
P ₂ O ₅	1	to 3
Diverse	0.5	to 1.0
Na ₂ O + K ₂ O	11	to 17
CaO + MgO	16	to 22
BaO	0	to 3
TiO ₂	0	to 2
Cr ₂ O ₃	0	to 0.5
Fe ₂ O ₃	0	to 1.5.

4. The mineral-fiber composition of any of claims 1 to 3, characterized in that the content of silicon dioxide is less than 55 percent by weight.

5. The mineral-fiber composition of any of claims 1 to 4, characterized in that the content of magnesium dioxide is more than 5 percent by weight.

6. The mineral-fiber composition of any of claims 1 to 5, characterized in that the content of magnesium dioxide is more than 6 percent by weight.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 95/02375

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00 C03C13/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 019 600 (OY PARTEK AB) 26 November 1980 see page 1, line 1 - page 4, line 34 ---	1-6
X	EP,A,0 399 320 (BAYER AG) 28 November 1990 see claims 1-3 ---	1-6
X	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 see page 2, line 1 - page 5, line 1 --- -/--	1-6

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☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/02375

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GLASTECHNISCHE BERICHTE, vol. 64, no. 1, January 1991 FRANKFURT DE, pages 16-28, XP 000178832 R. M. POTTER ET AL 'Glass Fiber Dissolution in a Physiological Saline Solution' see page 26, left column, paragraph 3 - page 27, left column; table 2 -----</p>	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. Application No

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